Journal of Organometallic Chemistry, 350 (1988) 251–256
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

A new route to $Fe_2Te_2M(CO)_6(PPh_3)_2$ (M = Ni, Pd, Pt) from $Fe_3Te_2(CO)_9$ and $M(PPh_3)_4$

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(Received February 5th, 1988)

Abstract

The synthesis, characterization and mechanism of formation of the mixed metal complexes, $Fe_2Te_2M(CO)_6(PPh_3)_2$ (M = Ni, Pd, Pt), from $Fe_3Te_2(CO)_9$ and $M(PPh_3)_4$ are described.

Introduction

Several main group elements have been successfully used to bridge metal atoms in the preparation of transition metal clusters [1]. The ability of these ligands to stabilize the metal framework makes them very useful in the building-up of such compounds. The lone pairs of electrons on the single atom ligands derived from the main groups act as an initial point of contact with the incoming metal fragments (eq. 1).

$$M_xE + M'_y \rightarrow M_x(\mu\text{-}E)M'_y \qquad (1)$$

Elements from group 16 have been widely used in the synthesis of a variety of such transition metal complexes, both homo- and hetero-nuclear [2]. For example, the sulfido ligand has been extensively used to bridge metal fragments in the stepwise synthesis of several osmium clusters and many mixed metal clusters. Although some selenium-containing clusters have also been reported, those containing tellurium have not attracted as much attention. Rauchfuss has reported the chemistry of some tellurium-containing iron carbonyl compounds [3], and has indicated that the reactivity of tellurium ligands will in fact be quite different from that of sulfur or selenium because of (i) the considerably larger size of tellurium (1.36 Å), and (ii) the greater Lewis acidity of tellurium. In contrast to the widespread use of $Os_3S_2(CO)_9$ as a starting block for the building of large nuclearity clusters, the complex $Fe_3Te_2(CO)_9$ shows very little reactivity towards addition of metal fragments. In an earlier report we stated that $PtFe_2Te_2(CO)_6(PPh_3)_2$ can conveniently be prepared from $Fe_3Te_2(CO)_9$ by treatment with $Pt(PPh_3)_4$ [4]. Here we discuss the generality of the reaction and the mechanism of formation of this type of compound.

Results and discussions

Stirring of a benzene solution of equimolar amounts of $Fe_3Te_2(CO)_9$ and $Pt(PPh_3)_4$ at room temperature gives the mixed-metal complex $Fe_2PtTe_2(CO)_6(PPh_3)_2$, (I) as well as some $Fe_3Te_2(CO)_7(PPh_3)_2$ (II) (eq. 2). The Ni and Pd analogues of the above complex are formed under these conditions when $Ni(PPh_3)_4$ and $Pd(PPh_3)_4$ are used instead of $Pt(PPh_3)_4$ (Table 1). Though the complex $NiFe_2Te_2(CO)_6(PPh_3)_2$ is isolable, it readily disproportionates in solution to give $Fe_3Te_2(CO)_8PPh_3$ along with some decomposition products. Attempts to use $Pt(C_2H_4)(PPh_3)_2$ as a source of the $Pt(PPh_3)_2$ fragment to prepare a mixed-metal complex from $Fe_3Te_2(CO)_9$ have been unsuccessful [5], but $PtFe_2Te_2(CO)_6(PPh_3)_2$ was obtained from the reaction of $Pt(C_2H_4)(PPh_3)_2$ with $Fe_2Te_2(CO)_6$ (eq. 3) [2]. It has been proposed that the addition of the $Pt(PPh_3)_2$ fragment across the Te–Te bond causes release of a considerable amount of FeTeTeFe ring strain in $Fe_2Te_2(CO)_6$, but in reaction 2 there is no such ring strain and so a different mechanism is expected for the formation of I from $Fe_3Te_2(CO)_9$. Although $Fe_3Te_2(CO)_9$ does not react with $Pt(C_2H_4)(PPh_3)_2$ in non-polar solvents, the reaction does take place slowly in benzene to give I [6]; this effect has been acounted for in terms of the fact that $Fe_2Te_2(CO)_6$ which is formed in polar solvents from $Fe_3Te_2(CO)_9$ is responsible for the formation of the complex I. Our observations reveal that I can be obtained from $Fe_3Te_2(CO)_9$ even in non-polar solvents when $M(PPh_3)_4$ (M = Pt, Pd, Ni) is used instead of $M(C_2H_4)(PPh_3)_2$ (M = Pd, Pt) as the source of $M(PPh_3)_2$ fragment (Scheme 1).

$$Fe_3Te_2(CO)_9 + Pt(PPh_3)_4 \rightarrow \underset{(I)}{Fe_2Te_2Pt(CO)_6(PPh_3)_2} + \underset{(II)}{Fe_3Te_2(CO)_7(PPh_3)_2} \tag{2}$$

$$Fe_2Te_2(CO)_6 + Pt(C_2H_4)(PPh_3)_2 \rightarrow \underset{(I)}{Fe_2Te_2Pt(CO)_6(PPh_3)_2} \tag{3}$$

$$Pt(C_2H_4)(PPh_3)_2 \xrightarrow{\text{solution}} Pt(PPh_3)_2 + C_2H_4 \tag{4}$$

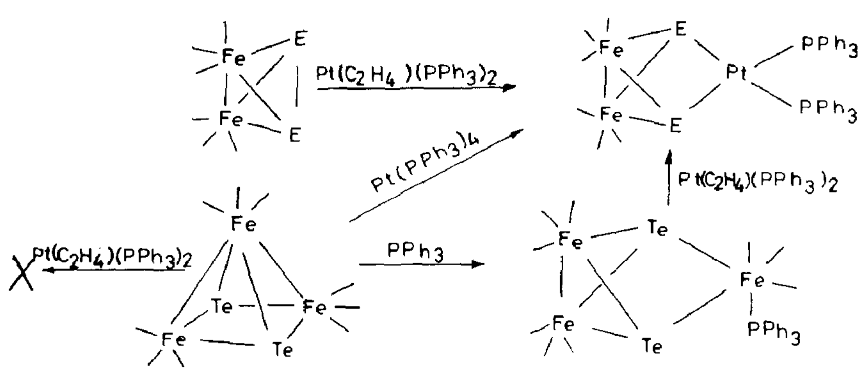
$$Pt(PPh_3)_4 \xrightarrow{\text{solution}} Pt(PPh_3)_3 + Pt(PPh_3)_2 + PPh_3 \tag{5}$$

In reaction 2, overall there is loss of an $Fe(CO)_3$ unit from $Fe_3Te_2(CO)_9$ and addition of a $M(PPh_3)_2$ fragment across the TeTe bond. Though both

Table 1

Infrared spectral data in the carbonyl region

Compound	$\nu(CO)$ (cm^{-1})	Solvent
$NiFe_2Te_2(CO)_6(PPh_3)_2$	2041(m), 2016(s), 1990(m)	Hexane
$PdFe_2Te_2(CO)_6(PPh_3)_2$	2033(s), 1992(s), 1958(s), 1948(sh)	CH_2Cl_2
$PtFe_2Te_2(CO)_6(PPh_3)_2$	2031(s), 1991(s), 1955(s), 1947(sh)	CH_2Cl_2
$Fe_3Te_2(CO)_7(PPh_3)_2$	2055(w), 2028(s), 1987(vs) 1966(sh), 1935(m), 1925(sh)	Hexane

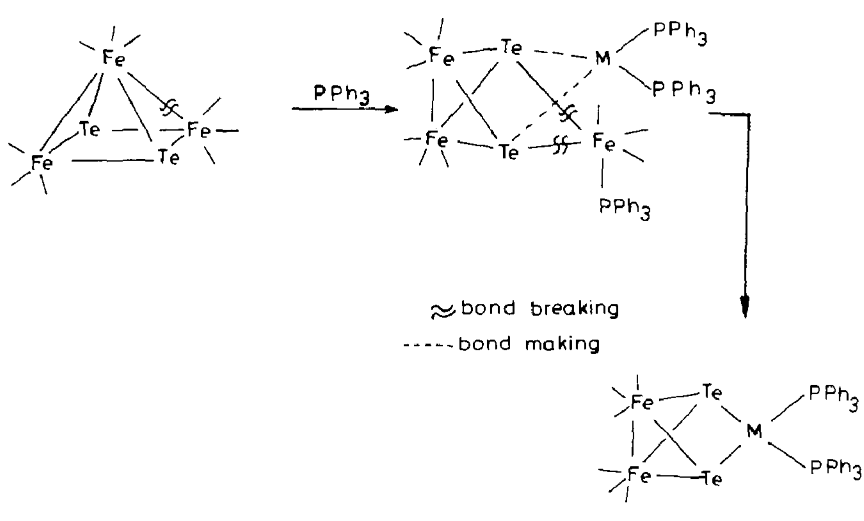


(III)

Scheme 1

$Pt(C_2H_4)(PPh_3)_2$ and $Pt(PPh_3)_4$ give $Pt(PPh_3)_2$ fragments in solution (reactions 4 and 5), the free PPh_3 ligand liberated in the case of the latter plays a significant role in the mechanism of formation of I. The reaction of $Fe_3Te_2(CO)_9$ with PPh_3 gives the adduct $Fe_3Te_2(CO)_9PPh_3$ (III). When $Fe_3Te_2(CO)_9PPh_3$ is treated with $Pt(C_2H_4)(PPh_3)_2$, the mixed-metal complex $Fe_2Te_2Pt(CO)_6(PPh_3)_2$ is formed in good yield, and so the reaction of $Fe_3Te_2(CO)_9$ with $Pt(PPh_3)_4$ must proceed via initial formation of the adduct $Fe_3Te_2(CO)_9PPh_3$ [3] followed by replacement of the $Fe(CO)_3PPh_3$ fragment of $Fe_3Te_2(CO)_9PPh_3$ by a $Pt(PPh_3)_2$ unit (Scheme 2).

The role of the heteroelement E in the structure and reactivity of Co_3E cluster has been discussed by Schmid [7]. The covalent radius of the heteroelement plays a significant part in determining the geometry of the cluster. The tricobalt structure assumes a closed nonacarbonyl or an open dodecacarbonyl structure depending upon the covalent radius of the heteroelement (Fig. 1a & 1b). The synthesis of $Co_3Te_2(CO)_9$ has not yet been achieved, and Lesch and Rauchfuss have suggested that tellurium occupies a borderline position in the tetrahedral transition-nonmetal cluster compounds (TMNMC) [3]. Using the similar arguments we can explain why



Scheme 2

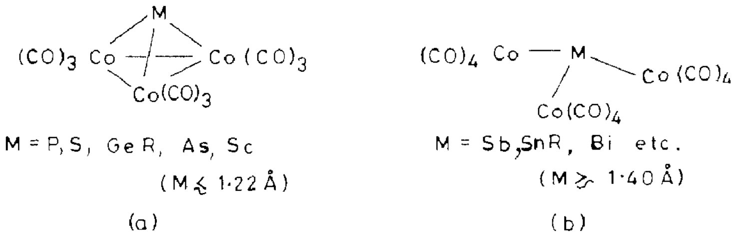


Fig. 1

$PtFe_2Te_2(CO)_6(PPh_3)_2$ and $PdFe_2Te_2(CO)_6(PPh_3)_2$ are formed in higher yields than the nickel analogue. The larger size of Pt (1.30 Å) and Pd (1.28 Å) compared with that of Ni (1.15 Å) would lead to opening of the cluster framework during substitution of the Fe fragment (Fe 1.17 Å), thus reducing some strain in the cluster framework. This would also account for the greater stability of the platinum and palladium complexes compared with that of the nickel analogue. Furthermore, the yield of $Fe_3Te_2(CO)_7(PPh_3)_2$, which is formed in all these reactions, increases on going from Pt to Ni in the triad. The high yield of $Fe_3Te_2(CO)_7(PPh_3)_2$ in the case of nickel suggests that formation of $NiFe_2Te_2(CO)_6(PPh_3)_2$ is less favoured. Our studies on the reactivity of $Fe_3Te_2(CO)_9$ incidates that the size of tellurium favours the formation of complexes with open structures.

The reactions of $Fe_3Te_2(CO)_9$ contrast with those of the related and much studied $Os_3S_2(CO)_9$. For instance $Os_3S_2(CO)_9$ reacts readily with $Pt(C_2H_4)(PPh_3)_2$ to form the mixed-metal clusters $Os_3S_2Pt(CO)_9(PPh_3)L$ (L = CO, PPh_3) [1] (see Fig. 2). The reaction of $Pt(PPh_3)_2$ fragment with osmium-sulfido cluster yields larger condensed products along with formation of new Pt–Os bonds [8]. In the case of tellurium-containing clusters the large size of tellurium prevents the formation of new metal–metal bonds and any new mixed-metal complexes are formed not via an initial contact of the incoming metal fragment with the tellurium but by substitution of a metal fragment in the original molecule. With appropriate metals, however, it may be possible to form closed type of clusters, and this possibility is under investigation.

Experimental

All reactions were carried out under dry nitrogen or argon by standard Schlenk techniques. All solvents were purified and dried before use. $Fe_2(CO)_9$ (Aldrich),

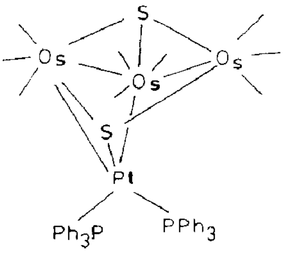


Fig. 2

Na_2TeO_3 (Lobachem), $Pt(PPh_3)_4$, $Pd(PPh_3)_4$ (Fluka) and $Ni(PPh_3)_4$ (Aldrich) were used as received. The infrared spectra were recorded on a 5DXB Nicolet FT IR spectrometer.

1. Preparation of $Fe_3Te_2(CO)_9$

The preparation of $Fe_3Te_2(CO)_9$ reported by Heiber and Gruber [9] was slightly modified. A solution of Na_2TeO_3 (7.3 g, 33 mmol) in water (50 ml) was added to a solution at 0 °C of $Fe_2(CO)_8{}^{2-}$ prepared from $Fe_2(CO)_9$ (1.5 g, 4 mmol) in methanol (30 ml) and 50% aqueous KOH. The mixture was stirred for about 1 h at room temperature, then cooled to 0 °C and neutralized with HCl (6 *M*). The resultant black precipitate was filtered off in air, washed with water, and dried in vacuo (30 °C) for about 12 h. The dry solid was then extracted with CH_2Cl_2 and purified by passage through a silica gel column with hexane as the eluent.

2. Reaction of $Fe_3Te_2(CO)_9$ with $Pt(PPh_3)_4$

A benzene solution (25 ml) of $Fe_3Te_2(CO)_9$ (100 mg, 0.15 mmol) was stirred with $Pt(PPh_3)_4$ (200 mg, 0.16 mmol) for 4 h at room temperature. The solvent was removed in vacuum and the red $PtFe_2Te_2(CO)_6(PPh_3)_2$ was separated from $Fe_3Te_2(CO)_7(PPh_3)_2$ on a grade II alumina column with 60/40 hexane/dichloromethane as eluent. Yield; $PtFe_2Te_2(CO)_6(PPh_3)_2$, 84%; $Fe_3Te_2(CO)_7(PPh_3)_2$, 16%.

3. Reaction of $Fe_3Te_2(CO)_9$ with $Pd(PPh_3)_4$

A benzene solution (25 ml) of $Fe_3Te_2(CO)_9$ (100 mg, 0.15 mmol) was stirred with $Pd(PPh_3)_4$ (180 mg, 0.15 mmol). Chromatography of the mixture on a grade II alumina column with 80/20 hexane/dichloromethane as eluent separated $PdTe_2Te_2(CO)_6(PPh_3)_2$ from the $Fe_3Te_2(CO)_7(PPh_3)_2$. Yield; $PdFe_2Te_2(CO)_6(PPh_3)_2$, 68.2%; $Fe_3Te_2(CO)_7(PPh_3)_2$, 18%.

4. Reaction of $Fe_3Te_2(CO)_9$ with $Ni(PPh_3)_4$

A benzene solution (25 ml) of $Fe_3Te_2(CO)_9$ (100 mg, 0.15 mmol) was stirred with $Ni(PPh_3)_4$ (170 mg, 0.153 mmol) at room temperature for an hour. The solvent was removed in vacuum and the mixture was transferred to a grade II alumina column. Three fractions were separated with hexane as the eluent. The black $Fe_3Te_2(CO)_8PPh_3$ came off first, followed by the orange-red $NiFe_2Te_2(CO)_6(PPh_3)_2$. The green compound $Fe_3Te_2(CO)_7(PPh_3)_2$, which is the major product of the reaction came off last. Yield: $NiFe_2Te_2(CO)_6(PPh_3)_2$, 20%; $Fe_3Te_2(CO)_8PPh_3$, 25%; $Fe_3Te_2(CO)_7(PPh_3)_2$, 54%.

5. Reaction of $Fe_3Te_2(CO)_9(PPh_3)$ with $Pt(C_2H_4)(PPh_3)_2$

A benzene solution (25 ml) of $Fe_3Te_2(CO)_9PPh_3$ (50 mg, 0.053 mmol) was stirred with $Pt(C_2H_4)(PPh_3)_2$ (slight excess) at room temperature for 1 h. The solvent was removed under vacuum and the product $PtFe_2Te_2(CO)_6(PPh_3)_2$ was isolated in good yield.

Acknowledgements

We are grateful to the Ministry of Science and Technology, Government of India, New Delhi for financial support.

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